Prescribed Analytical Protocol (PAP)

Volume 4 (PAP-4)

Analyte Group 4 (Particulate Air Analyses)

Revision: June 2021

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Exhibit A: Summary of Basic Contract requirements

Overview of Analyte Group - The data from the analytes in Group 4 are used for several purposes including for comparisons to ambient air quality standards, detection of trends over time and to provide data for use in health assessments. The overall program guidance comes from EPA regulation and guidance which is periodically subject to change. The EPA revisits criteria monitoring standards, monitoring programs and analytical methods for criteria pollutants at least every five years. It is possible that during the period of this contract, Federal regulations could require a modification of an analysis method, a minimum detection limit or a data handling convention. Potential contract awardees must be aware of the possibility that changes in the contract requirements may be necessary and that the NYSDEC will work with the Contractor to see that the program meets Federal requirements.

This analyte group involves the micro gravimetric analysis of ambient air samples for particulate matter of size fractions less than 2.5 and less than 10 microns (PM2.5 and PM10) using the requirements given in 40 CFR Parts 50, 53, and 58. Laboratories working in this analyte group will also be required to analyze collected airborne particulate matter on filter media for optical carbon, respirable silica and selected metals by EDXRF and ICPMS using EPA IO- Series, NIOSH and Federal Reference Methods. The Laboratories performing work within this analyte group will be required to have applicable NELAC or ISO/IEC certification, equipment, personnel, and knowledge to analyze samples in accordance with the requirements set forth in the Method Documentation provided in Exhibit D.

Overview of PM-2.5 and PM-10 Gravimetric Analyses - The Contractor shall conduct micro gravimetric weighing of PM2.5 filter elements supplied by the NYSDEC, load the pre-weighed filters into NYSDEC provided sampling equipment and ship and receive these samples from up to 10 specific NYSDEC field locations. The contractor is required to track each filter by serial number through the process and to meet all of the specified timelines and filter equilibration environmental conditions in order to meet EPA monitoring requirements. The Contractor shall also conduct micro gravimetric weighing of filter elements after these samples have been received from NYSDEC field locations and equilibrated in a suitable chamber to determine the net loading of each sample. All filter handling and weighing procedures, as well as associated QA/QC measures, shall be conducted by the Contractor in accordance with PAP-4 Exhibits and EPA's regulatory requirements ("Reference Method for the Determination of Fine Particulate Matter as PM2.5 in the Atmosphere," outlined in Federal Register 40 CFR Part 50, Appendix L, and the guidance provided by EPA's Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II, Part II, Section 2.12.)[1] The EPA provides a template that summarizes the gravimetric program requirements which can be found on the Ambient Monitoring Technology Information Center webpage: https://www3.epa.gov/ttnamti1/

Overview of Optical Carbon Analyses – The Contractor shall analyze selected filters using a SootScan TM Transmissometer (http://www.mageesci.com/) before the pre-sample weighing and after the post sampling weighing is completed. The SootScanTM Transmissometer determines

[1] Guidance Document 2.12 Monitoring PM2.5 in Ambient Air Using Designated Reference or Class I Equivalent Methods revised January 2016.

the amount of light transmitted (or attenuated) through the filter media using two wavelengths (370 nm and 880 nm).

Overview of Elemental Analyses - The Contractor shall conduct filter preparation, extraction if required and analysis by EDXRF or ICPMS for specified filters containing ambient particulate matter to determine filter loadings of metals. NYSDEC will provide the filters for these analyses. The laboratory must follow all sample preparation requirements as detailed in the applicable method documentation provided in Exhibit D. Any requests for special sample processing made in a NYSDEC Quality Assurance Project Plan (QAPP) or similar NYSDEC-approved project specific documentation shall supersede the requirements of the method documentation and those listed in PAP-4.

Overview of Respirable Silica Analyses – The Contractor shall conduct filter preparation, extraction and analysis by XRD (X-Ray Powder Diffraction) for specified filters containing ambient particulate matter to determine filter loadings of crystalline quartz, cristobalite and tridymite. The contractor shall provide the filters for these analyses. The laboratory must follow all sample preparation requirements as detailed in the applicable method documentation provided in Exhibit D

Equipment, Facilities & Instrumentation - The gravimetric analyses for PM-2.5 and PM-10 samples have tight timelines for both the pre-weighing and post weighing procedures. The laboratory must have redundant facilities for the equilibration and post-weighing of filters in order to prevent the invalidation of samples due to the failure to meet USEPA Federal Method requirements. The contractor does not need redundant instrumentation for the metals or optical carbon analyses providing that the work can be accomplished within the required time. These analyses are performed in batches and the contractor has 60 days to complete the work after the filters are received.

The contractor's facilities must also include secure refrigerated filter archive space large enough to maintain NYSDEC's gravimetric, and EDXRF samples for the duration of the contract. These samples must be available for future analytical or research needs and archived filters must be easily located and provided on a filter serial number basis at no charge to the NYSDEC. The extracts prepared for ICPMS metals analysis must be archived for six months.

The specifications for the balances and conditioning chamber for micro gravimetric analyses can be found in the EPA document: EPA's Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II, Part II, Section 2.12. A summary of EPA requirements (must) and recommendations (should) for equipment, facilities and instrumentation follows:

A. Microbalance Requirements and Recommendations

1. The microbalance must have a readability and repeatability of ±1μg.
2. The microbalance must have a unique identification number and be calibrated upon installation as well as annually and the calibration must be checked prior to each weighing session.
3. The microbalance must be located in a controlled environment, as described below.

4. The microbalance should be located on a clean, vibration-free surface.
5. The microbalance should be located in an environment free of air pulses or turbulence which might prolong or disrupt efforts to achieve stable weights.
6. The microbalance should be electrically grounded to reduce static.
7. The microbalance should be left on at all times.
8. The microbalance should be maintained and operated strictly according to the manufacturer's instructions.
9. The microbalance should utilize electronic data reporting to avoid transcription and keystroke errors. If a PC is used to record the data, a LED monitor should be used and not a CRT which creates static charge.
10. The laboratory should have service agreement with a local balance company for routine independent calibrations (recommended every 6 months; or minimally every 1 year) and service calls.

B. Analytical Instrumentation in Addition to the Microbalance

1. The laboratory must maintain a calibrated ICPMS for the analysis of specified elements.
2. The lab must maintain a calibrated XRF analyzer for the analysis of Pb and other specified elements.
3. The lab must maintain a calibrated Magee SootScan™ Model OT21 transmissometer for the analysis of optical carbon.
4. The lab must maintain a calibrated XRD for the analysis of crystalline quartz, cristobalite and tridymite.

C. Controlled Environment Requirements

1. The mean temperature must be maintained within 20-23º C.
2. The standard deviation of the 5 minute temperature data must be within ±2º C over the 24 hour period prior to the weigh session.
3. The mean relative humidity must be within 30-40%.
4. The standard deviation of the 5 minute relative humidity data must be within ±5% RH over the 24 hour period prior to the weigh session.
5. Temperature and humidity data must be collected from a calibrated sensor and recorded at least every 5 minutes on a continuous basis. The sensors must have NIST traceable calibrations and their calibration must be checked at least every 6 months.
6. The data handling system for the environmental chamber must have a way to produce reports for the analyst to verify that weigh room conditions are acceptable for the 24 hour period prior to and during each weigh session. The data system should be designed to warn analysts if conditions do not meet specifications for this program.
7. Heating and Air Conditioning set points in the weigh chamber should be maintained at all times including weekends.
8. The weigh chamber should have slightly positive air pressure in order to minimize dust entrainment from spaces outside of the chamber.

D. Filter Conditioning and Weighing Requirements

1. Filters must be tracked by serial number and conditioned in the controlled environment for a minimum of 24 hours prior to weighing. The EPA recommends limiting the equilibration period to no more than 72 hours in order to minimize the potential for contamination. The date and time when filters enter and exit the weigh chamber must be documented.
2. Filters must be inspected for defects prior to use. A light box is suitable for this purpose.
3. Filters must be conditioned in the same controlled environment in which the balance is kept.
4. Both pre- and post-sampling weighing should be carried out on the same balance, preferably by the same analyst.
5. The relative humidity during the post-sample weighing must be within ±5% of pre-sampling weighing.
6. The lab must weigh lot blanks to ensure that each batch of filter media are stable. The cost to weigh these filters is not billable under this contract.
7. The lab must weigh additional lab blanks to ensure that lab conditions are not affecting gravimetric analysis. The cost to weigh these filters is not billable under this contract.
8. Field blanks must be included in routine sample preparation and analysis. These must be randomly sent to field locations at a frequency of 1 filter per shipment for the gravimetric monitoring programs. The cost to weigh these filters is billable under this contract.
9. The pre-sampling weighing must be carried out within 30 days of the scheduled sampling period.
10. The lab must check the temperature of the filters when they arrive from field locations. An infrared non-contact thermometer is suitable for this purpose. Since the filters are shipped overnight with cold packs (ice substitutes) the arrival temperature is assumed to be the warmest the filters were since leaving the field locations.
11. The post-sampling weighing must be carried out within 10 days after the end of the sampling period, unless the filter is maintained at 4 C or less during the time between retrieval from the sampler and the start of the conditioning, in which case the period shall not exceed 30 days.
12. The lab must have NIST certified primary standards which are used to check the mass of working standards which are used during each weigh session.
13. The lab must utilize a technique to neutralize static charges on the sampling filters. In order to remove static electricity from filters, direct exposure to Polonium 210 strips and or an ionizer is recommended. Polonium 210 strips should be replaced according to the manufacturer's instructions, usually within 6 months from date of manufacture. For further guidance see: *Cahn Technical Note: Static Control for Balances*, 6/90. This document is available within the U.S. EPA's Ambient Monitoring Technology Information Center (AMTIC) PM monitoring information web page.

E. Filter Storage Requirements

1. The NYSDEC will provide filters for this program that have met the EPA QA specifications for the PM-2.5 and PM-10 FRM and elemental analysis programs.

2. The laboratory must inventory and keep filters owned by the NYSDEC separate from other customer's filters.
3. The laboratory must monitor the inventory of new filters and notify the NYSDEC when the supply of new filters represents approximately 1 month of normal usage.
4. Filters returned from field locations must be stored refrigerated between 1-4º C prior to conditioning in the weigh chamber.
5. Once the filters have gone through weighing and other required analyses, filters must be archived, refrigerated on petri slides using a serial number or barcode identification system.
6. Filters must be made available by request from the NYSDEC at no additional charge to the NYSDEC.
7. The filters must be archived for the length of the contract.

Certifications and Licenses - At this time, New York's ELAP certifications do not cover low volume gravimetric analysis as specified in 40 CFR Part 50, Appendix L or metals analysis by EDXRF or by ICPMS or respirable silica. If the New York ELAP program includes these analyses in the future, the contract laboratory would have to become accredited for these analyses within 12 months or face loss of this contract. The NYSDEC requires labs to have either applicable NELAC or IHLAP accreditation for the analyses under this contract.

Invoice Format Requirements – Invoices must include information necessary to identify the vendor, the vendor's tax identification number, the contract the vendor is working under and the date range for the work billed on the invoice. The sample information must include:

Filter serial numbers (arranged in numeric order)
Batch associated with Filter delivery: (Gravimetric samples only)
Date filters received: (ICPMS, Silica, XRF and XRF Pb only)
Analysis performed: (Gravimetric, Optical Carbon, Silica, ICPMS, XRF, XRF Pb only)
Breakdown of cost per filter and total for the invoice

Invoices must not include cost to analyze samples which are deemed invalid due to lab error. Invoices also must only include one type of analysis. These invoices can be sent together but they must be able to be referenced separately.

NYSDEC Equipment Maintenance - The magazines and cassettes provided by the NYSDEC for use in the gravimetric PM-2.5 and PM-10 program are re-used. These must be cleaned and maintained by the lab on an as needed basis. The NYSDEC will provide magazine fittings and O-rings as needed. The lab is also responsible for providing the insulated (foam lined) cardboard shipping boxes and substitute ice packs that are included in the outgoing shipments so that the filters can be returned cold.

Data Ownership - The data collected or produced for the NYSDEC under this contract is the sole property of the NYSDEC and cannot be released without the express consent of the NYSDEC.

Exhibit B – Report Requirements

Overview - The Group 4 analytes are for on-going monitoring programs so the data reporting requirements are based on Federal air quality monitoring programs. These requirements tailor the data so that the NYSDEC can electronically process the data and quality assurance information into formats acceptable to the EPA.

Weekly Summary Reports – The Contractor must submit weekly reports summarizing the activity associated with this contract for the week prior. The weekly report must include the shipping and batch information for the samples received and sent to the field locations in the prior week. The report must also include a status of the on-going project activities with specific mention of any issue that could affect the quality control or sample or data delivery dates. The weekly reports for Analyte Group 4 must be transmitted via e-mail to the individuals specified in the IFB.

The NYSDEC reserves the option to eliminate the requirement for the Weekly Summary Reports for Group 4 analytes if the Agency decides that they are unnecessary to insure adequate oversight of the contractor's performance. The contractor will be notified if the Agency decides to waive this requirement.

Data Reports: **Gravimetric PM-2.5, PM-10 and Optical Carbon -** Results should be reported on a Monthly basis in electronic format. The data must be provided in a consistent Excel file format to permit automated computer input of data files. The contractor is required to send identical locked and unlocked copies of each data file. The unlocked file format permits the NYSDEC to load the data into other data processing software. The locked version of the file permits the NYSDEC to verify the accuracy of the original data sent from the contract lab. The table below includes the information that needs to be in each monthly data report. The NYSDEC will provide an example of acceptable data files if requested.

File 1: Data Required for each Filter in Excel Columns

Filter ID Number
Lot Number
Initial RH (%)
Initial Temp (Deg C)
Initial Weigh Date
Initial Weight (mg)
Duplicate Initial Weight (mg)
Cassette number
Magazine Batch number
Blank Y/N
Date Mailed to Field
Date Returned
Temp Upon Receipt (Deg C)
Date Range for Equilibration
Final Weigh Date, Temp, RH%
Final Weight (mg)
Duplicate Final Weight (mg)
Net Mass Filter Loading (mg)
Data Flags and Comments

File 2: Data Required for Each Day Filters are in Environmental Chamber

Chamber Identification
Temp Deg C (ea. 5 minute average)
RH % (ea. 5 minute average)
Temp Deg C (daily average)
RH % (daily average)

File 3: Data Required for Each Weigh Session

Analyst Name
Date, Time Start, Time End
Balance ID, Robot if applicable
Transmissometer ID
RH %, Temp^{o} C: Initial, End
Standard Weight 1, 2 mg
Standard Weights determined
Standard Weights after 10 samples
Lab Grav Blanks Initial / Final
Lab Carbon Blanks Initial / Final
Field Blanks Initial / Final
Filter Lot Blank for Session

File 4: Data Required for Each Monthly Report

Files as noted above
Description of issues including: shipping, handling, conditioning or any other issue or defect that could affect data validity

Data Reports: Optical Carbon – Results should be reported on a Monthly basis in electronic format. The data must be provided in a consistent Excel file format to permit automated computer input of data files. The contractor is required to send identical locked and unlocked copies of each data file. The unlocked file format permits the NYSDEC to load the data into other data processing software. The locked version of the software permits the NYSDEC to verify the accuracy of the original data sent from the contract lab. The table below includes the information that needs to be in each monthly data report. The NYSDEC will provide an example of acceptable data files if requested.

Data Required for Each Optical Carbon Analysis Batch (Optical Attenuation) (46.2 mm Teflon Filters)
Analyst Name, Transmissometer ID
Date and Time (pre-sample and post sample)
Filter Serial Number(s) and Lot Number
IR Attenuation and UV Attenuation (pre-sample and post sample)
QA parameters
Blank filter and Lot stability IR Attenuation and UV Attenuation
Duplicate analysis of sample filter (1 in 20 minimum frequency)

Data Reports: XRF 31 Elements and XRF Pb only - Results should be reported within two months of when the filters are received. The reports must be in electronic format. The table below includes the information that must be included in each file. The NYSDEC will provide an example of acceptable data files if requested.

Data Required for Each EDXRF Elemental Analysis Batch (PM-10 Pb by EDXRF: 40 CFR part 50 Appendix Q) (46.2 mm Teflon Filters)
Analyst Name, EDXRF ID
Date
Filter Serial Number(s)
Filter Lot Number(s)
Concentration in ng/cm^2 of: Lead/Element by EDXRF
Concentration in ng/filter of: Lead/Element by EDXRF (sample area: 11.86 cm^2)
Minimum Detection Limit in ng/filter of: Lead/elements
QA parameters
Blank filter spectra and correction for same lot of filters as samples
Standard Reference Material: Calibration Standards on filter Media or film
Spiked Standard Reference Material: Standards on Media or film (with % recovery) (Include spiked sample filter and clean unsampled filter media)
Duplicate analysis of sample filter (1 in 20 minimum frequency)

Data Reports: ICPMS Elements - Arsenic, Beryllium, Cadmium, Lead, Manganese, Nickel, Antimony, Cobalt, Selenium, Vanadium: Results should be reported within two months of when the filters are received. The reports must be in electronic format. The table below includes the information that needs to be in each file. The NYSDEC will provide an example of acceptable data files if requested.

Data Required for Each ICPMS Analysis Batch
Analyst Name, Date of analyses
Filter Serial Number(s)
Concentration in ng/filter of: Arsenic, Beryllium, Cadmium, Lead, Manganese, Nickel, Antimony, Cobalt, Selenium, Vanadium
Minimum Detection Limit in ng/filter of: Arsenic, Beryllium, Cadmium, Lead, Manganese, Nickel, Antimony, Cobalt, Selenium, Vanadium
QA parameters
Blank: Initial and Continuing Calibration Check
Standard Initial and Continuing Calibration Check
Reagent Blank (each analyte)
Reagent Blank Spike at specified concentration (each analyte)
Standard Reference Material: High Purity Standards Trace Metals on Filter Media
Duplicate analysis of extracted filter (1 in 20 minimum frequency)
Serial Dilution typically 1 in 5 (1 in 20 minimum frequency)

Data Reports: Respirable Silica – Results should be reported on a Monthly or batch basis depending on the number of submitted samples in electronic format. The data must be provided in a consistent Excel file format to permit automated computer input of data files. The contractor is required to send identical locked and unlocked copies of each data file. The unlocked file format permits the NYSDEC to load the data into other data processing software. The locked version of the software permits the NYSDEC to verify the accuracy of the original data sent from the contract lab. The table below includes the information that needs to be in each data report. The NYSDEC will provide an example of acceptable data files if requested.

Data Required for Each Respirable Silica Analysis Batch (XRD Analysis) (47 mm PVC Filters)
Analyst Name, XRD ID
Date and Time of Analyses
Filter/Sample Identification Number(s) and Lot Number
Mass on Filter: quartz, cristobalite and tridymite, MDL for each analyte
QA parameters
Field Blank data if sample provided, Lot blank data and QC results for XRD
Duplicate analysis (1 in 20 minimum frequency)

Exhibit C CRQL requirements

CRQL Overview – For Group 4 analytes the NYSDEC utilizes the term MDL (Minimum Detection Limit) to make the program results consistent with EPA program guidelines. The NYSDEC requires that the actual data be reported for all samples regardless if these values are above or below the lab's current MDL. The data reported below MDL must be flagged with a QA qualifier. As an example, the EPA has provided the following table to show the flagging procedures for NATTs (ICPMS) metals data.

If Concentration is	Value to Report	Flag Applied
> SQL	Value	None
> MDL ≤ SQL	Value	SQ
≤ MDL	Value	MD
Not Detected	0	ND

Gravimetric Analysis PM-2.5 and PM-10 - This is a measurement by difference so there is no SQL or MDL, however, replicate and comparisons to gravimetric standards must be reported as specified in 40 CFR Part 50, Appendix L. All data is to be reported including negative values.

Optical Carbon Analyses – The IR and UV values from sampled filters are compared to pre sample values from the same filters prior to sampling. The resultant data is a measurement by difference so there is no SQL or MDL, however, replicate and comparisons to neutral density (optical standards when they are available) must be reported. All data is to be reported including negative values.

XRF Elements (Pb and 31 Elements) – The EPA method IO-3.3 has a procedure to calculate the MDL for EDXRF. The reference for the MDL determination is:

> EPA Protocol IO-3.3, Section 12.
> Reference: *Compendium Method IO-3.3, Determination of Metals in Ambient Particulate Matter Using X-Ray Fluorescence (XRF) Spectroscopy,* U.S. EPA Center for Environmental Research Information, Office of Research and Development, Cincinnati, OH, June 1999.

The MDL is determined using the following calculation:

$$\text{detection limit for element I} = 2\delta_i = \frac{2(2B_i)^{1/2}}{s_i t}$$

B_i is the background counts for element I,
s_i is the sensitivity factor for element I
t is the counting live time

The calculated MDLs must be equal to or lower than the MDLs specified in the analyte group 4 price table. The NYSDEC does not expect the "un-sampled" filter blank concentrations of any elements to be significant in comparison to the contractor's MDL. These filters are Quality

Assured by the EPA and the EPA's Quality Assurance protocols include certification of very low filter blanks for elements. The contractor must report the filter blank data and immediately notify the NYSDEC if filter blanks are greater than the MDL for any element.

ICPMS Elemental Analyses – The MDLs must be reported with each batch of filters analyzed. The MDL must be determined at least once a year unless the analytical instrument has undergone a major service or repair in which case the MDL determination must be re-run.

Method detection limits are determined according to the procedures of 40 CFR Part 136 Appendix B. However, for metals that are measured in the filter blanks at concentrations greater than three times the estimated MDL, seven to 10 replicate blank filters should be analyzed to determine the MDL values (40 CFR Part 136, Appendix B found at: http://www.epa.gov/waterscience/methods/det/. The NYSDEC does not expect the blank concentrations of any elements to be significant in comparison to the contractor's MDL. These filters are Quality Assured by the EPA and this Quality Assurance includes certification of very low filter blanks for elements. The contractor must report the filter blank data and immediately notify the NYSDEC if filter blanks are greater than 50% of the MDL for any element.

To calculate an MDL first determine if concentrations in the blank filters are below the estimated MDL, then the filters should be spiked, digested and fortified at a concentration of two to five times the estimated MDL. The extracts must then be analyzed and the results used in the calculations below. The minimum MDLs that must be achieved are shown in the Group 4 price table.

The MDL is calculated as follows: $MDL = (t) \times (S)$

t = Student's t value for a 99 percent confidence level and a standard deviation estimate with n - 1 degrees of freedom [t = 3.14 for seven replicates]

S = standard deviation of the replicate analysis.

The EPA is proposing an alternate method to determine MDLs for ICPMS for the NATTs program. If this method is selected and is listed in a revised NATTs Technical Assistance Document (TAD), the contractor will have to provide MDLs calculated using this method. Additionally, the MDLs must be equal to or lower than the MDLs specified in the analyte group 4 price table.

Respirable Silica Analyses - The MDLs must be reported with each batch of filters analyzed. The MDL must be determined at least once a year unless the analytical instrument has undergone a major service or repair in which case the MDL determination must be re-run. Additionally, the laboratory must report calibration results including recoveries and estimated measurement uncertainty and bias.

Exhibit D – Approved Methods

Gravimetric PM-2.5 and PM-10 - The methods for the Group 4 analytes are based on Federal Air Monitoring requirements. The analytical method for the Gravimetric PM-2.5 and PM-10 program is Micro-Gravimetry. The specifications for this method can be found in "Reference Method for the Determination of Fine Particulate Matter as PM-2.5 in the Atmosphere," as specified in Federal Register 40 CFR Part 50, Appendix L. The following two EPA documents provide a summary of the Federal Method Requirements:

http://www.epa.gov/ttn/amtic/files/ambient/pm25/qa/m212covd.pdf
http://www.epa.gov/ttn/amtic/files/ambient/pm25/qa/valdtmpl.pdf

The method utilizes 47 mm Teflon filters which are Quality Assured for this purpose by the EPA. These filters will be procured by the NYSDEC and provided to the contractor. The micro-balance must at a minimum have a sensitivity of 1.0 µg and a range of (0 – 5000 µg). The data must be reported in µg/filter.

Optical Carbon Analyses – Currently, there is no accepted federal method for measuring the attenuation of light through Teflon sampling filters. This data is being collected and compared to data collected using other Carbon analysis methods. The contractor must operate the SootScan TM Transmissometer (http://www.mageesci.com/) according to the manufacturer's instructions and provide the data and necessary QA information as specified in exhibit B.

XRF Elements (Pb and 31 Elements) – This analysis utilizes EPA method IO-3.3. for the Pb PM-10 and for the elemental analysis program (31 metals from the EPA CSN list) by EDXRF. The method is an approved Federal Reference Method and can be found in CFR Appendix Q to Part 50.

> Reference: *Compendium Method IO-3.3, Determination of Metals in Ambient Particulate Matter Using X-Ray Fluorescence (XRF) Spectroscopy,* U.S. EPA Center for Environmental Research Information, Office of Research and Development, Cincinnati, OH, June 1999.

The program utilizes 47 mm Teflon filters which are Quality Assured for this purpose by the EPA. These filters will be procured by the NYSDEC and provided to the contractor. The potential range of elemental concentrations is less than the range of particulate matter on a sampling filter (0 – 200 $\mu g/m^3$) and the reporting units are ng Element/filter.

ICPMS Elemental Analyses - The analytical method must satisfy the requirements of the National Air Toxics Trends Stations (NATTs) program and the Pb NAAQS. Currently the program utilizes IO-3.5 ICP-MS for the analysis of Arsenic, Beryllium, Cadmium, Lead, Manganese, Nickel, Antimony, Cobalt, Selenium and Vanadium.

The program utilizes 47 mm Teflon filters which are Quality Assured for this purpose by the EPA. These filters will be procured by the NYSDEC and provided to the contractor. The contract lab will also have to extract the filters using a NATTs or Pb FRM acceptable method which could include:

Heated ultrasonic water bath – EQL-0510-191
80 ± 5°C with 1.02M nitric/2.23M hydrochloric acid

Hot block digestion – EQL-0710-192
95 ± 5°C with 3.5% nitric (v/v)

The entire 47 mm Teflon filter including the support ring must be digested for this analysis and the potential range of elemental concentrations is less than the range of particulate matter on a sampling filter (0 – 200 $\mu g/m^3$) and the reporting units are ng Element/filter.

Respirable Silica Analyses – The specified method is NIOSH 7500 silica, crystalline by XRD (filter redeposition). The contractor must supply suitable 47 mm PVC filters for use in the NYSDEC's sampling cassettes, magazines and samplers. The filter size and the field portion of the method will be modified to the extent that the particle size will be PM-10, the sample volume will be 24 m^3 and the results will be applicable to ambient air.

Exhibit E – Quality Assurance/Quality Control

Gravimetric PM-2.5 and PM-10 – The NYSDEC requires that the lab prepares an acceptable Quality Assurance Project Plan (QAPP) conforming to EPA format and SOPs for the tasks involved in completion of the analysis and sample handling. The QAPP must identify and satisfy all of the sample handling and QA activities outlined in the methods specified in Exhibit D. The Contractor shall submit the QAPP and SOPs to NYSDEC within 15 calendar days of receipt of the Notice to Proceed. NYSDEC will require revisions to the QAPP if the QAPP conflicts with the Statement of Work (SOW), applicable laws, EPA regulations and references included in the SOW. The lab must also reanalyze samples that do not meet QA/QC criteria at no cost to the NYSDEC. This includes samples that do not meet precision QA requirements. Samples that fail QA/QC criteria will not be billable to the Department.

The data reports must include the quality assurance information specified in Appendix B as well as the identification of any samples that failed QA/QC requirements as well as the cause of the failure. The lab must meet all of the sample handling and analysis criteria and produce valid data for at least 95% of the samples.

The Contractor must also participate at no cost to the NYSDEC in periodic performance evaluation and comparison activities as requested by the NYSDEC and or the USEPA. The contractor must receive a satisfactory or higher rating for the inter-comparison or risk forfeiture of the contract. The Performance Evaluation Program (PEP) conducts an external assessment of both sample collection and gravimetric analysis. The NYSDEC Quality Assurance staff perform the sample collection portion of the PEP program and this activity does not involve the gravimetric contract laboratory. The EPA's National Air and Radiation Environmental Laboratory (NAREL) conducts semi-annual gravimetric inter-laboratory comparison studies as part of its quality assurance support of EPA's Office of Air Quality Planning and Standards (OAQPS). The purpose of the gravimetric studies is to evaluate EPA and State laboratories that weigh Teflon filters used for the determination of PM-2.5 collected with Federal Reference Method (FRM) ambient air samplers.

Optical Carbon Analyses – An explanation of the operation of the SootScan TM Transmissometer (http://www.mageesci.com/) must be included in the Contractor's QAPP and SOPs must be provided. Quality Assurance data as specified in exhibit B must be provided in monthly data reports.

XRF Elements (Pb and 31 Elements) – The NYSDEC requires that the lab prepares an acceptable Quality Assurance Project Plan (QAPP) conforming to EPA R5 format and SOPs for the tasks involved in completion of the analysis and sample handling. The QAPP must identify and satisfy all of the sample handling and QA activities outlined in the methods specified in Exhibit D. The Contractor shall submit the QAPP and SOPs to NYSDEC within 15 calendar days of receipt of the Notice to Proceed. NYSDEC will require revisions to the QAPP only if the QAPP conflicts with the Statement of Work (SOW), applicable laws and EPA regulations, and references included in the SOW. The lab must also reanalyze samples that do not meet QA/QC criteria at no cost to the NYSDEC. This includes samples that do not meet precision QA requirements. Samples that fail QA/QC criteria will not be billable to the Department.

The data reports must include the quality assurance information specified in Appendix B as well as the identification of any samples that failed QA/QC requirements as well as the cause of the failure. The lab must meet all of the sample handling and analysis criteria and produce valid data for at least 95% of the samples.

The Contractor must also participate at no cost to the NYSDEC in periodic performance evaluation and comparison activities as requested by the NYSDEC and the USEPA. The contractor must receive a satisfactory or higher rating for the inter-comparison or risk forfeiture of the contract. The EPA's National Air and Radiation Environmental Laboratory (NAREL) or a contractor conducts periodic inter-laboratory comparison studies as part of its quality assurance support of EPA's Office of Air Quality Planning and Standards (OAQPS). The purpose of the comparison studies is to evaluate EPA, Contract and State laboratories that analyze filters used for the determination of Pb and elemental composition in federally supported monitoring programs.

ICPMS Elemental Analyses - The NYSDEC requires that the lab prepares an acceptable Quality Assurance Project Plan (QAPP) conforming to EPA format and SOPs for the tasks involved in completion of the analysis and sample handling. The QAPP must identify and satisfy all of the sample handling and QA activities outlined in the methods specified in Exhibit D and the Technical Assistance Document (TAD) Document for the National Air Toxics Trends Stations (NATTs) Program. The Contractor shall submit the QAPP and SOPs to NYSDEC within 15 calendar days of receipt of the Notice to Proceed. NYSDEC will require revisions to the QAPP only if the QAPP conflicts with the Statement of Work (SOW), applicable laws and EPA regulations, and references included in the SOW. The lab must also reanalyze samples that do not meet QA/QC criteria at no cost to the NYSDEC. This includes samples that do not meet precision QA requirements. Samples that fail QA/QC criteria will not be billable to the Department.

The data reports must include the quality assurance information specified in Appendix B as well as the identification of any samples that failed QA/QC requirements as well as the cause of the failure. The lab must meet all of the sample handling and analysis criteria and produce valid data for at least 95% of the samples.

The Contractor must also participate at no cost to the NYSDEC in periodic performance evaluation and comparison activities as requested by the NYSDEC and the USEPA. The contractor must receive a satisfactory or higher rating for the inter-comparison or risk forfeiture of the contract. The EPA's National Air and Radiation Environmental Laboratory (NAREL) or a contractor conducts periodic inter-laboratory comparison studies as part of its quality assurance support of EPA's Office of Air Quality Planning and Standards (OAQPS). The purpose of the comparison studies is to evaluate EPA, Contract and State laboratories that analyze filters used for the determination of Elemental composition in federally supported monitoring programs.

Respirable Silica - The NYSDEC requires that the lab prepare an acceptable SOP for the tasks involved in completion of the analysis and sample handling.

The data reports must include the quality assurance information specified in Appendix B as well as the standards analysis and the identification of any samples that failed QA/QC requirements as well as the cause of the failure. The lab must meet all of the sample handling and analysis criteria and produce valid data for at least 95% of the samples.

Exhibit F – Chain of Custody

Introduction - The Gravimetric low volume PM-2.5 and PM-10 program requires the lab to load the pre-weighed filters into cassettes, prepare chain of custody forms and field data forms and labels for the magazines with cassette numbers, filter serial numbers and use by dates. The cassettes have to then be loaded into magazines for shipments to up to ten specific field locations. The cassette and filter serial numbers batch number and use by dates are printed by the contractor on Avery labels and a copy of this label is attached to the tag on the magazine and to the field Data Form which is then wrapped around each sampler magazine. The Chain of custody forms are wrapped around each magazine as well before the shipment is sent to the field locations from the lab.

The NYSDEC provides the filters, cassettes and magazines for use during the contract period. The filters must be stored in Petri dishes or Petri slides that are provided by the laboratory except during the equilibration period. Once the final weights have been determined, OC value determined and the EDXRF analysis has been performed, if applicable, the filters on the Petri slides or dishes must be stored in a secure refrigerated environment.

The lab is also responsible for determining the temperature of the PM-2.5 and PM-10 filter shipment upon delivery to the lab. This should be done by using an infrared thermometer to determine the temperature of the uppermost magazine in the shipping box and by assigning that temperature for all of the filters in the shipment.

Chain of Custody Forms - The NYSDEC requires chain of custody for the environmental samples because they are shipped from the lab to field locations and back. This information is collected on the chain of custody form which is reproduced in this Exhibit. These forms must be retained by the lab along with the filters until the filters are ultimately returned to the NYSDEC. The NYSDEC requires the contract lab to formally take possession of filters for analysis but does not require specific chain of custody within the lab or during transit via the NYSDEC's selected commercial carrier. The NYSDEC does require notification of sample shipment tracking information when shipments are sent to specified field locations. The labels on the magazines and the Field Data Forms must be prepared by the lab and shipped to field locations with each batch. The Field Data Forms are retained by field staff for data processing by the NYSDEC.

Storage and Archive Requirements – The NYSDEC requires that sampled filters are stored at temperatures from 0° C to 4° C for five years from the end of the year in which the samples were collected. During this time the filters or a selection of filters by serial number must be made available to the NYSDEC by request and at no charge to the NYSDEC. At the end of this period the filters must be returned to the NYSDEC. The filters do not have to be refrigerated at the end of the five year on-site storage period.

The filter extracts that are prepared for the ICPMS analysis must be retained by the laboratory for 6 months. These must be available in case a follow-up analysis is necessary due to a QA issue.

Internal chain of custody requirement for samples - Internal (within laboratory) chain of custody is not required for the Group 4 samples as long as the pre and post weighing time requirements are met.

PM-2.5 and PM-10 Chain of Custody Form

Samples Handled for the New York State Department of Environmental Conservation

Part I. Filter Weighing and Shipping Information

Analyst Name: Weighing Date:
Project No.: Shipment Date
Shipped Via:

Filter ID	Filter Cassette No.	Filter Expiration Date	Sample Date	Valid? (Yes/No)

Part II. Field Site/Field Data

Field Technician_____

Filter #1 Refrigerated within 177 Hours? _____

Filter #2 Refrigerated within 177 Hours? _____

Filter #3 Refrigerated within 177 Hours? _____

Filter #4 Refrigerated within 177 Hours? _____

Comments for Lab Staff _____

Part III-Weighing Laboratory

Received by: _____Date Received _____

Shipment Integrity OK? Yes____ No____ Describe_____

Arrival (max) temperature_____

If Found: Please Return to NYSDEC BAQS
625 Broadway Albany, NY 12233-3256
518-402-8508

NEW YORK STATE DEPARTMENT OF ENVIRONMENTAL CONSERVATION

Division of Air Resources, Bureau of Air Quality Surveillance
625 Broadway, Albany, New York 12233-3256
P: (518) 402-8508 | F: (518) 402-9035
www.dec.ny.gov

Reviewed By: _____

Problem Noted:

PM-2.5 ☐ PM-10 ☐ Field Data Sheet:

Site Name and Number _____

Sampler: Pri____ Dup____ Serial# NY2025IW_____ Operator_____

	Filter #	Cassette#	Use By Date	Sample Date	Flags & Status
#1	_____	_____	___/___/___	___/___/___	#1 _____
#2	_____	_____	___/___/___	___/___/___	#2 _____
#3	_____	_____	___/___/___	___/___/___	#3 _____
#4	_____	_____	___/___/___	___/___/___	#4 _____

Batch # & Sample Dates Blank: Yes_____ No_____

Date Filter #1 Removed From Sampler:_____ Less Than 177 Hrs:_____

Date Filter #2 Removed From Sampler:_____ Less Than 177 Hrs:_____

Date Filter #3 Removed From Sampler:_____ Less Than 177 Hrs:_____

Date Filter #4 Removed From Sampler:_____ Less Than 177 Hrs:_____

Date of last VSCC Cleaning/Exchange: _____ (PM-2.5 Only - Clean Monthly)

Date of Last Instrument Data Download: _____ (Download Twice Monthly)

Sampler Flags, Status Conditions, Power Outages: _____

Notes and Observations: _____

_____

If cassette #3 (1/3 site) or cassette #4 (daily site) contains a filter, it is to be run as a blank. Enter the filter and cassette # into the sampler's filter list screen after the other two and check the blank "Y". The empty spacer cassette should be programmed as 999999 for the filter and cassette number and should be programmed as blank "Y".